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It is well known that block copolymers composed of incompatible polymers have multiphase structure, each component polymer being separated into its own phase, and their multiphase structure leads to unusual physical properties. In particular, block copolymers composed of a soft polymer as the major component and a hard polymer as the minor component can have elastomeric properties since the hard polymer blocks from different molecules segregate into hard domains dispersed in the soft matrix of the soft polymer blocks and

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the hard domains serve as crosslinking and reinforcement. Some block copolymers of this nature are now successfully used as thermoplastic elastomers.

Block copolymers also exhibit unusual melt rheological properties, notably very high viscosity and elasticity in comparison to the component homopolymers of equal molecular weight. The unusual melt rheological properties have been attributed to the remnants of the multiphase structure which persist far above the glass transition or melting points of the component polymers.

We found in this project that an experimental styrene-butadiene-styrene block copolymer upon heating exhibited a relatively sharp melt rheological transition at a very high temperature from unusually high viscoelastic behavior to the normal behavior expected of homopolymers. We also found using transmission electron microscopy, that the SBS sample underwent a morphological transition from multiphase structure to single-phase structure at a temperature corresponding to the melt rheological transition. Our findings clearly show that block copolymers can retain their multiphase structures to very high temperatures and their unusual melt rheological behavior comes from the multiphase structure in the melt.

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Foreword

Block copolymer technology offers an opportunity to obtain unique poly-
meric materials of exceptional properties ranging from high impact rigid
polymers to high modulus elastomers through controlled synthesis and process-
ing. The unique characteristics of block copolymers come from their multiphase
structure which strongly depends on the chemical make-up and processing history.
This project has made a step forward in understanding the development of multi-
phase structure in block copolymers and the relationship between the rheological
property and the structure in the molten state. The support of this project
by the Army Research Office is sincerely appreciated.

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INTRODUCTION

Block copolymers composed of imcompatible blocks have multiphase structure, each component being separated into its own phase. For example, the polystyrene blocks and the polybutadiene blocks in styrene-butadiene-styrene (SBS) block copolymers separate into their own phases. If polystyrene is the minor component of a SBS block copolymer, the polystyrene phase becomes hard domains imbedded in soft matrix of the polybutadiene phase. The hard polystyrene domains composed of polystyrene chain ends from different molecules act as physical crosslinks conferring to the SBS block copolymer elastomeric properties. Some SBS block copolymers and other block copolymers of the same nature are now commercially used as thermoplastic elastomers.[1-3]

Because of the theoretical interest in the multiphase morphology of block copolymers as well as the industrial importance in block copolymers as thermoplastic elastomer, the research efforts on block copolymers have been quite extensive in the recent years and one can make a long list of the articles published on block copolymers. However, the proceedings[4-8] of the five symposia on block copolymers and multi-component polymers sponsored by the American Chemical Society in 1967, 1969, 1970, 1974 and 1978 will provide sufficient references for the purpose of this report. Estes, Cooper and Tobolsky[9] published a review paper on block copolymers and related heterophase elastomers. The Army Materials and Mechanics Research Center sponsored a symposium on block and graft copolymers in 1972.[10] Most recently, in late August 1979, Midland Macromolecular Institute held an International Symposium on Block Copolymers.

The two-phase structure in block copolymers has been clearly demonstrated by electron microscopy[4A-D,5A-C,6A-D,11,12], small angle x-ray scattering[5D,6E], thermal analysis[4C,5E-H,13], small angle light scattering[6E,6F,14], polarized light[5B], dynamic mechanical relaxation[4C,4E,5F,5I,5J,15-17], birefringence[4F,5K,18-20], and infrared dichroism[6G], etc. The marked effects of preferential solvents on the morphology of block copolymers have been well established[4C,5A-D,5J,6A,6B,6H,6I,12,21]. These investigations have shown that the average domain size is of the order of 100 $\overset{o}{A}$ - 300 $\overset{o}{A}$ and that the morphology and the domain structure depend strongly on the condition of sample preparation. For example, Beecher, et al[4C] showed, using electron micrograph and mechanical property evidences, that Kraton 101 sample (a SBS block copolymer with about 28 wt. % polystyrene) cast from benzene/heptane mixture had a polybutadiene continuous phase but the same sample cast from methyl-ethyl-ketone/tetrahydrofuran mixture had a polystyrene continuous phase. The domain structure of a block copolymer can vary from spheres to rods to plates, as shown in Figure 1, depending on the casting solvents and conditions[4C,5A,6A,6B,6D,], as well as on the composition and molecular weight[4B,4C,4E,5A,5B,5F,5J,6A,6C]. Different block length distributions can cause wide changes in the domain morphology at a constant overall monomer composition.[8A] Thermal treatment[5C,5L] or mechanical[4C,4G,4M,22,23] treatment can also alter the morphology. Different morphological structures give different mechanical and relaxation properties[4B,4C,5F,5J,6A,6I,8A]. The theoretical aspects of the phase separation in block copolymers have been studied using statistical thermodynamic principles of different degrees of complexity by a number of investigators[4A,4H,24-26]. These theories can predict the onset of phase separation and in some cases the resulting morphology in terms of molecular and

thermodynamic variables.

Block copolymers not only exhibit unusual physical properties at use temperatures near room temperature but also exhibit unusual melt rheological properties at high temperatures of processing often causing processing difficulty. Although there have been numerous investigations on the morphology, the morphology/property relationship and the theory of phase separation at use temperature, relatively a small number of investigations have been reported on the melt rheology and especially the structure/property relationship in the molten state.

The main objective of this project was to investigate the structural features of the melt of an experimental SBS sample responsible for the unusual melt rheological behavior. A secondary objective was to assess the accuracy of the various theories proposed for the multiphase structure of block copolymers. The results of this investigation will contribute to better understanding of the structural development in block copolymers during processing and hopefully to controlled processing history for obtaining particular structures/properties.

MELT RHEOLOGY OF BLOCK COPOLYMERS-LITERATURE REVIEW

Block copolymers often show unusually high melt viscosity and elasticity at processing temperatures, causing processing difficulties. Such unusual melt rheologcial properties are generally attributed to the remnants of the multiphase structure which persists far above the glass transition or melting temperatures of the component homopolymers[4E,27-33]. It is also expected that, analogous to semi-crystalline polymers, the morphology and thus the properties of block copolymers will depend on the processing conditions since the morphology of block copolymers is found to depend on thermal and mechanical treatments.

Holden, Bishop and Legge[4E], and Kraus and Gruver[27] were among the first to investigate the melt rheology of block copolymers. Holden, et al., observed the following very unusual flow behavior with SBS block copolymers.

1. The viscosities of SBS block copolymers at low shear rates go through a pronounced maximum and then decrease as the styrene content is increased. In other words, the viscosities of these materials can be greater than the viscosities of either of the homopolymers of the same molecular weight, even at temperatures well above the glass transitions of both homopolymers.

2. The viscosities of SBS block copolymers (at constant composition) at the relatively low shear rate of about 0.1 sec^{-1} are proportional to the molecular weight raised to a power of about 5.5 Since none of the block copolymer samples showed Newtonian behavior (i.e., viscosity independent of shear rate) at the shear rates examined, the exponent at lower shear rates would be even higher than 5.5 This high exponent deviates substantially from the well known exponent of 3.5 at zero shear condition (or lower as shear rate is increased) for linear polymers.[34,35]

3. SBS block copolymers of intermediate styrene contents (39,53 and 65 wt. %) at $150^{\circ}C$ show two distinct viscosity-shear rate relationships. This indicates that two different flow mechanism can exist and the flow mechanism depends on the shear conditions applied to the melt.

4. The apparent flow activation energy of a SBS block copolymer decreases sharply and continuously with increasing temperature from $100^{\circ}C$ and $200^{\circ}C$. This indicates that the flow mechanism

is continuously changing with temperature from 100°C to 200°C.

These flow properties are entirely different from those of homopolymers and random copolymers. Our laboratory recently reported similar observations[30,31]. Holden, et al., suggested a two-phase structured system existing in the melt, probably a weaker version of the well defined multiphase structure at lower temperatures, in order to explain these unusual flow properties. One can expect from the probable two-phase structure in the melt that block copolymer melts would exhibit strong elastic responses and the elastic response would be sensitive to any change in the structure of the melt. One can also expect that the high elasticity of block copolymer melts would cause problems in processing. Melt flow instability (or melt fracture) is generally attributed to the elasticity of the melt.[36,37] Unfortunately, Holden, et al., did not discuss the elastic properties of the block copolymer melts.

Kraus and Gruver[27] studied the viscosities of random and $(A-B)_n$ type block copolymers of styrene and butadiene. The random copolymers showed Newtonian behavior up to a shear stress of 10^6 dynes/cm^2 and satisfied the shear rate-temperature superposition giving a constant apparent flow activation energy over the temperature range examined. On the other hand, the block copolymers showed non-Newtonian behavior (i.e., viscosity increased as shear rate was decreased) even at low shear stress and did not satisfy the shear rate-temperature superposition. They also concluded that remnants of the multiphase structure in the block copolymers appeared to persist to quite high temperatures.

Krause, Naylor and Rollmann[28] studied the steady-state and dynamic viscosity of liner [(A-B-A) type] and star-branched block copolymers of styrene and butadiene. They made the following observations.

1. At constant molecular weight and total styrene content, viscosities are greater for polymers terminating in styrene blocks.

2. To a surprisingly good approximation, the length of the terminal blocks, not the total molecular weight, governs the viscoelastic behavior of these block copolymers.

3. These block copolymers exhibit strongly non-Newtonian flow behavior over the entire range of shear rates $(0.5\text{-}50 \text{ sec}^{-1})$ and frequencies (22-690 radians/sec) studied.

In addition, their viscosity vs. molecular weight figures showed that the viscosity dependence on molecular weight for these block copolymers was unusually great and changed with molecular weight. They also rationalized the unusual melt rheology of these block copolymers in terms of a two-phase structure which persisted to a significant degree in the melt.

Karoly[5N] studied the melt viscosity of a poly(α)-methylstyrene-polyisoprene-poly(α)methylstyrene at 200°C and 230°C. He noted that the melt viscosities were high and the extrudates showed severe melt fracture even at 200°C and shear rates as low as 1.8 sec^{-1}, an indication of high elasticity.

Erhardt, O'Malley and Crystal[5I] studied the viscoelastic properties of (A-B) and (A-B-A) type block copolymers of ethylene oxide (A) and styrene (B) at low frequencies and low shear rates using a Weissenberg Rheogoniometer[38] and a modified Vibron viscoelastometer[39]. Their findings on the viscosities of these block copolymers confirmed those of Holden, et al.[4E] None of these block copolymers showed Newtonian behavior at low shear rates of frequencies. Their findings on the elasticities of these copolymers should be noted:

1. The (A-B) block copolymer shows a high elasticity even at
   high temperatures while both homopolymers or blends of
   the homopolymers do not show appreciable elasticity at
   high temperatures.

2. The elasticity of the (A-B) block copolymer up to 200°C
   depends on the solvent casting conditions of the sample.
   This is a definite indication that the difference in mor-
   phology can be retained up to very high temperatures.

Matzner, Noshay, and McGrath[40] investigated the structure/processa-
bility/property relationships for organo-siloxane block copolymers.
(Although many organo-siloxane block copolymers possess very attractive
properties, the problem of extremely high melt viscosity precludes
their value in practical applications.) They could find a qualitative
correlation between the processability and the differential solubility
parameter of the segments in organo-siloxane block copolymers. Their
correlation indicated that the differential solubility parameter should
be about one or less for acceptable processability. It will be of interest
to extend their correlation to other block copolymer systems and to quanti-
tatively correlate the differential solubility parameter with the rheolog-
ical response.

Arnold and Meier[29] studied the dynamic viscosities of several SBS
block copolymers as a function of frequency using a Weissenberg Rheogonio-
meter. The SBS block copolymer exhibited two distinct regions; a low
frequency region where the viscosity continually and sharply increased
with decreasing frequency and a high frequency region where the viscous
response was similar to those of the homopolymers. They suggested that
the multiphase morphology in (A-B-A) type block copolymers would be essen-
tially intact even at high temperatures and thus the melt rheology would

be dominated by the interplay of processes tending to disrupt and to re-form the domain systems. According to their theory, (A-B-A) type block copolymer melts are expected to exhibit a network response including a yield stress at very low shear rates and thus Newtonian behavior cannot be expected for (A-B-A) type block copolymers as long as the multiphase structure is retained in the melt.

Brown and Witsiepe[2] studied the melt viscosity of segmented polyester-polyurethane (E-U) block copolymer. Their results showed that the flow behavior of the segmented E-U block copolymer was different from those of other block copolymers discussed above. The segmented E-U block copolymer showed Newtonian behavior and relatively low viscosity at low shear rates below 10 sec^{-1}. One might suspect from such flow behavior that their segmented E-U block copolymer sample did not retain the multiphase struc-ture at high temperatures.

THEORY OF PHASE SEPARATION IN
BLOCK COPOLYMERS - A BRIEF REVIEW

If the phase separated state of a block copolymer is taken as the reference state, the change in Gibbs free energy resulting upon mixing of the different phases to form a homogeneous single-phase is given by

$$\Delta G = \Delta H - T \cdot \Delta S$$

where ΔH is the enthalpy change and it will be positive as long as the com-ponent polymers are thermodynamically incompatible. ΔS is the entropy change and it will also be positive since the randomness of the molecules increases upon mixing. T is the temperature. Mixing will occur if ΔG is negative. As T is increased, ΔH and ΔS do not change as much as T itself and thus the entropy term ($T \cdot \Delta S$) will increase faster than the enthalpy term (ΔH). ΔG will eventually become zero at a temperature $T_p = \Delta H/\Delta S$ to be called the phase transition temperature, and the block

copolymer will undergo a phase transition from the multiphase structure to the single-phase structure at Tp.

A number of thermodynamic and statistical thermodynamic theories have been proposed to predict the phase separation behavior in block copolymers. The most prevalent theories are those of Fedors[4H,41], Krause[24,42], Meier[4A,43-45], Leary and Williams[25,46,47], and Helfand[26,48-54]. Detailed discussion of these theories is outside the scope of this report. We will simply state that these theories differ in the complexity of calculating ΔH and ΔS. Simple theories (Fedors, Krause) can only predict the stable state (single-phase vs. multiphase) whereas complex theories (Meier, Leary and Williams, Helfand) can predict the domain structure as well as the stable state. ΔH is usually expressed in terms of a thermo-dynamic interaction energy parameter, notably the solubility parameter difference between the component polymers. ΔS is usually calculated from chain statistics, and the complexity of calculating ΔS depends on the level of sophistication of the assumed multiphase structure. One problem in the theoretical treatment of the multiphase structure in block copolymers comes from the mathematical difficulty of calculating ΔS. Another problem comes from the difficulty of obtaining an accurate solubility parameter difference between the component polymers since solubility parameter cannot be directly measured for polymers. Helfand avoids the use of solubility parameter difference by introducing a new "energy parameter". Helfand's energy parameter may be defined with a less uncertainty than solubility parameter difference but its probable error is still large enough to significantly change the prediction of the theory (as shown later). Recalling that the separation temperature can be expressed as Tp = $\Delta H/\Delta S$, Tp will be over-estimated by any theory which over-estimates ΔH or under-estimates ΔS. Simple theories do not consider as many entropic effects as complex theories and thus yield a lower value of ΔS and consequently predict a

higher Tp for a given value of ΔH.

EXPERIMENTAL

The experimental SBS sample was an anionically polymerized, experimental material provided by Shell Chemical Company. It has 7,000 styrene block molecular weight and 43,000 butadiene molecular weight (25.4% polystyrene content). The microstructure of the polybutadiene block was 40% cis-1,4, 50% trans-1,4 and 10% 1,2. The polymer in the form of foamy crumb was dissolved in cyclohexane and filtered to remove large foreign particles. The recovered polymer, after evaporating off the solvent, was molded into a thin sheet in a vacuum oven at about 120°C.

The melt rheological properties of the sample were measured using a Weissenberg Rheogoniometer in dynamic mode. Cone and plate having 5 cm diameter and 4° angle were employed. The electron microscope specimens were prepared by first subjecting the sample to a desired thermal history of annealing or quenching (in liquid nitrogen), staining (and hardening) by bromine, embedding in epoxy, and finally microtoming. Micrographs were taken using a JEOL-1000S electron microscope at 100 kV accelerating portential at 35,000 X magnification. The image was further magnified 2.86 X during printing.

RESULTS AND DISCUSSION

Figures 2 and 3 present the dynamic viscosity ($\eta '$) and dynamic modulus (G') of the SBS sample at 11 temperatures. $\eta '$ is very shear sensitive over entire test frequencies at low temperatures, but limiting zero-shear viscosity at low angular frequencies (ω) is noted at high temperatures in Figure 2. The sample exhibits high G' as shown in Figure 3, and a sharp drop in G' at low ω is noted between 138.5 and 142.5°C. $\eta '$ and G' at 11 temperatures are superimposed in Figures 4 and 5,

respectively, taking $138.5^{\circ}C$ as the reference temperature. All data are superimposed onto a single master curve at high ω, but two characteristic branches are found at low ω. The upper branches below $138.5^{\circ}C$ exhibit a high pseudoplasticity and elasticity while the lower branches above $157^{\circ}C$ exhibit a limiting zero-shear viscosity with negligible elasticity. When η', G' and phase angle at a given test ω are replotted as a function of temperatures using the data presented in Figures 2 and 3, these figures clearly show that the sample undergoes a relatively sharp melt theological transition in the temperature region between 140 and $150^{\circ}C$ from a highly viscoelastic, nonlinear behavior to a behavior typical of a homogeneous melt including the limiting zero-shear viscosity.

The unusual melt rheological behavior of block copolymers has been attributed to the remnants of the multiphase structure persisting far above the glass transition or melting points of the component polymers[30-33]. The relatively sharp, melt rheological transition between 140 and $150^{\circ}C$ far above the glass transition temperature of the polystyrene domain, observed with the SBS sample indicates an accompanying morphological transition from a multiphase structure to a single-phase structure rather than a gradual weakening of the polystyrene domains. In order to ascertain this hypothesis, direct morphological observations were made of the sample.

Figures 6A and 6B are the electron micrographs of the SBS sample annealed at $120^{\circ}C$, clearly showing a two-phase structure. The dark portion represents polybutadiene phase selectively stained by bromine and the light portion corresponds to polystyrene phase. These micrographs reveal the equilibrium structure of the SBS sample at $120^{\circ}C$ to be cylindrical polystyrene domains more or less regularly arranged in a hexagonal array in a polybutadiene matrix. The diameter of the polystyrene rods is about $150\overset{\circ}{A}$ and the distance between the centers of the rods is about $300\overset{\circ}{A}$.

Such structure gives approximately 23% polystyrene volume fraction, in excellent agreement with the calculated value based on the polystyrene content. Figure 7 shows the structure of the sample quenched from 125°C. The multiphase structure observed in Figure 6 is virtually preserved in this sample. However, the samples quenched from 170 and 190°C showed no structure as shown in Figure 8. The very tiny grain in Figure 8 is similar to what is observed with carbon samples. Multiphase structure could be restored in the quenched samples when the quenched samples were annealed at 125°C before staining as shown in Figure 9. The electron microscope results clearly show that the SBS sample has a multiphase structure below the melt rheological transition at about 150°C but a single phase structure above the melt rheological transition. Furthermore, it is apparent that the rate of phase formation in the bulk sample is sufficiently slow to prevent a multiphase structure upon quenching.

TEST OF THEORIES

It is possible to use the phase transition temperature, Tp of the SBS sample as a criterion to assess the accuracy of the various theories discussed previously. We have programmed the five different theories of Fedors, Krause, Meier, Leary and Williams, and Helfand into a computer, and their predictions of Tp for the SBS sample are presented in Figures 10 and 11. (The observed phase transition was relatively sharp, and thus the domain structure could be assumed to be intact up to Tp as a first approximation in the theoretical calculations.) Each theory contains at least one ambiguous parameter and thus a number of different predictions can be made by each theory depending on the choice of the ambiguous parameter such as shown for the Krause theory in Figure 10 as an example. Aside from such ambiguity, it is clear from Figures 10 and

11 that the predicted Tp critically depends on the value of the thermodynamic interaction energy parameter (the solubility parameter difference in Figure 10 and the energy parameter in Figure 11). The experimental Tp of about 420°K could be predicted by all of the theories by adjusting the interaction energy parameter within the range of reported literature values. Therefore, the Tp value of one sample was not sufficient to assess the accuracy of the theories. However, a number of Tp values measured for several different samples would serve as a criterion to assess the accuracy of the theories since a theory should be able to predict the correct Tp values for the samples using the same set of input parameters including the interaction energy parameter.

CONCLUSION

Block copolymers composed of incompatible component polymers can have attractive physical properties owing to their multiphase structures. The multiphase structure in these block copolymers often persists to very high temperatures of processing causing processing difficulties due to extremely high viscosity and elasticity.

Our investigation with an experimental SBS sample revealed that a morphological transition from a multiphase structure to a single-phase structure occurred over a relatively narrow temperature region far above the glass transition of the polystyrene phase, and that a corresponding melt rheological transition from a highly viscoelastic, nonlinear behavior to a typical behavior of single-phase polymers occurred as a result of the morphological transition.

All of the thermodynamic theories proposed for the phase separation behavior in block copolymers could be made to correctly predict the phase transition temperature of the SBS sample by adjusting a parameter in each theory within the range of possible values. However, measurement of the

phase transition temperatures for a number of controlled SBS samples is necessary to critically examine the accuracy of these theories due to the extreme sensitivity of their preditions on the uncertain values of the parameter.

Our research will be continued to include a series of SBS samples with systematic variations in molecular weight, composition and block length.

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A	A	A, B	B	B
SPHERES	CYLINDERS	LAMELLAE	CYLINDERS	SPHERES

Increasing A - Content

⟶

Decreasing B - Content
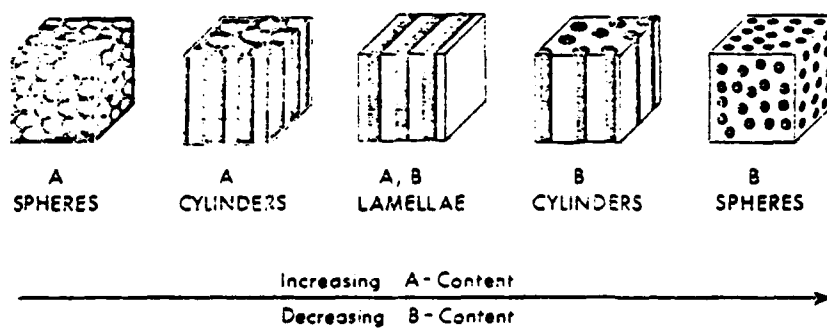
Figure I.　Schematic Representation of Five
Possible Microdomain Structures
of Block Copolymers (From Ref. 6)
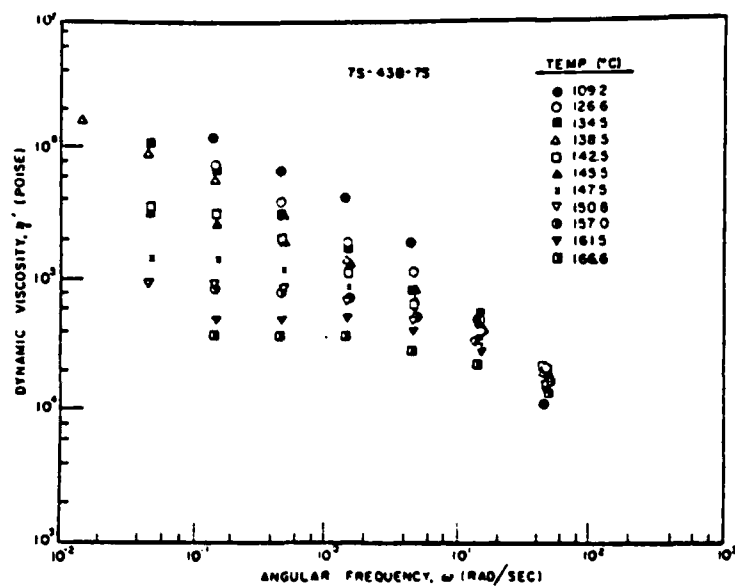
Figure 2.   Dynamic Viscosity as a Function of Angular
             Frequency.
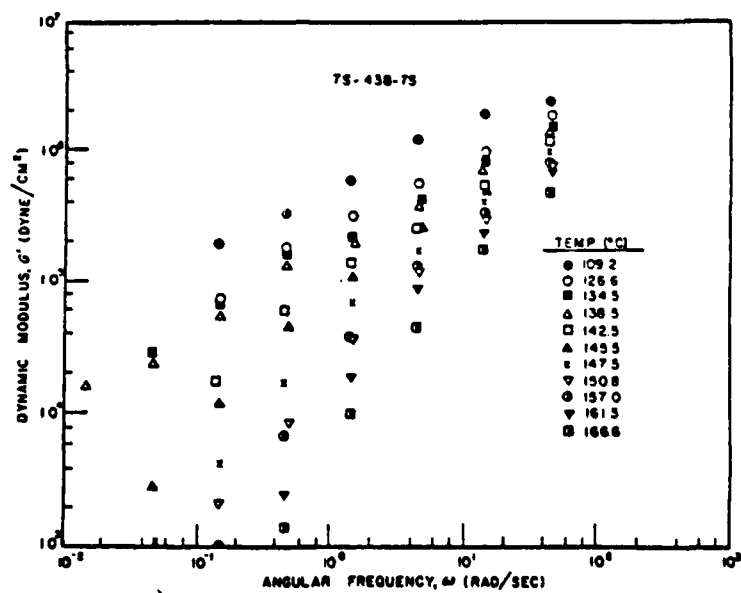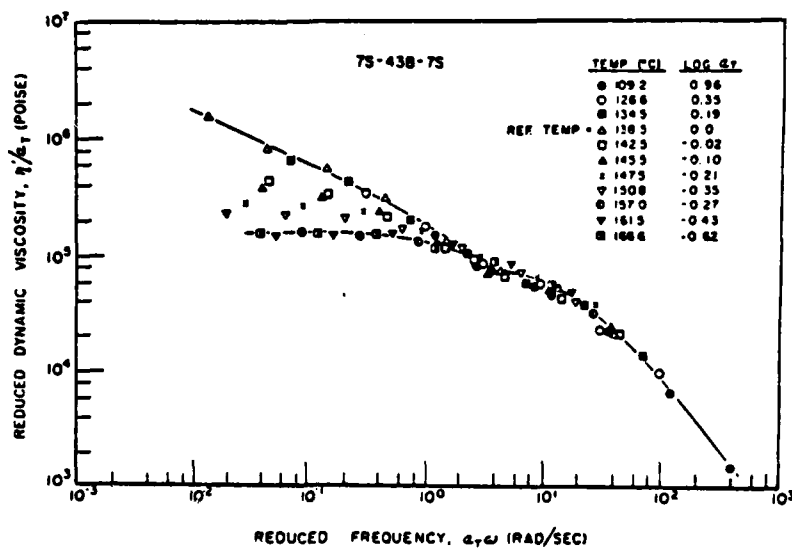

Figure 3.   Dynamic Modulus as a Function of Angular
             Frequency.

Figure 4.   Reduced Dynamic Viscosity as a Function of
            Reduced Frequency.
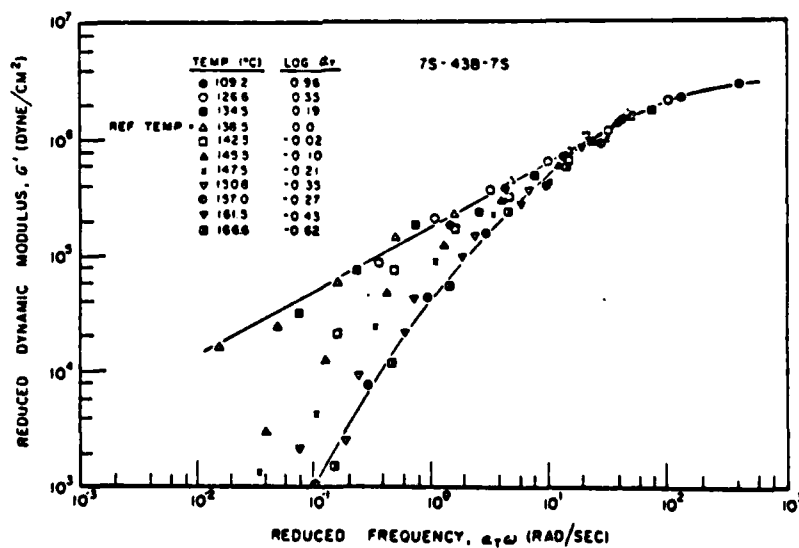
Figure 5.   Reduced Dynamic Modulus as a Function of
            Reduced Frequency.
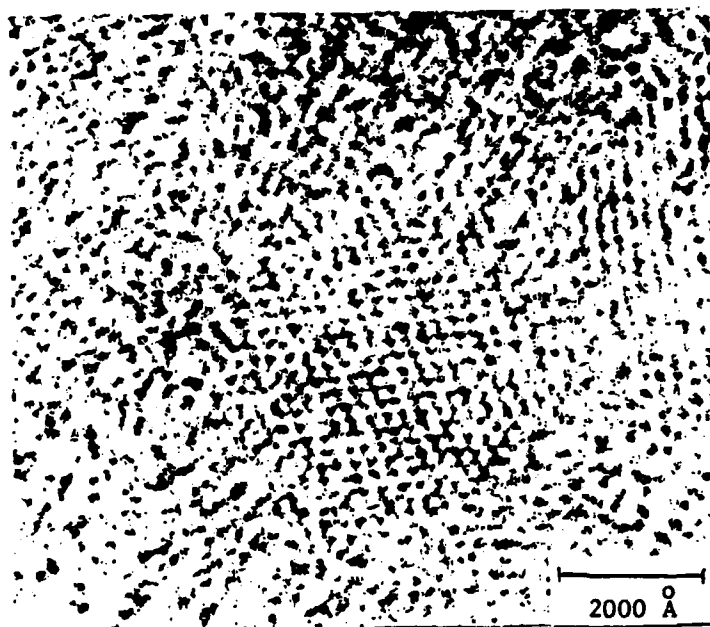
(A)
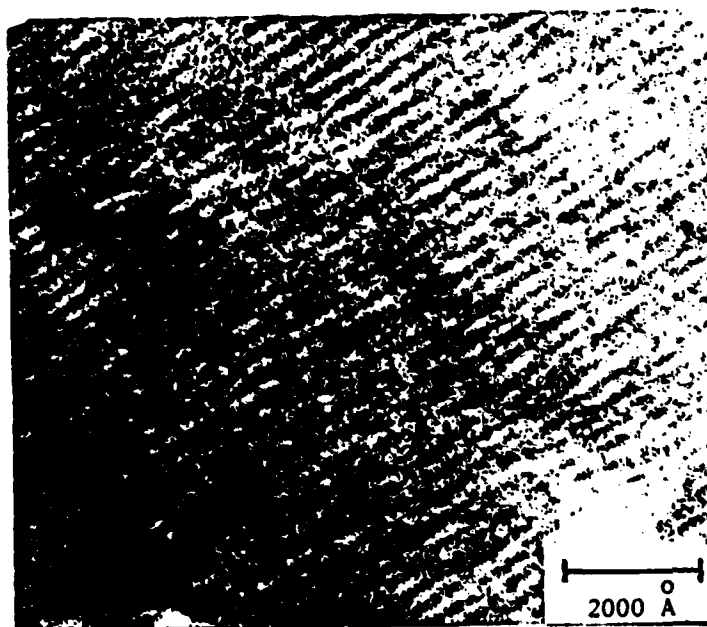
(B)

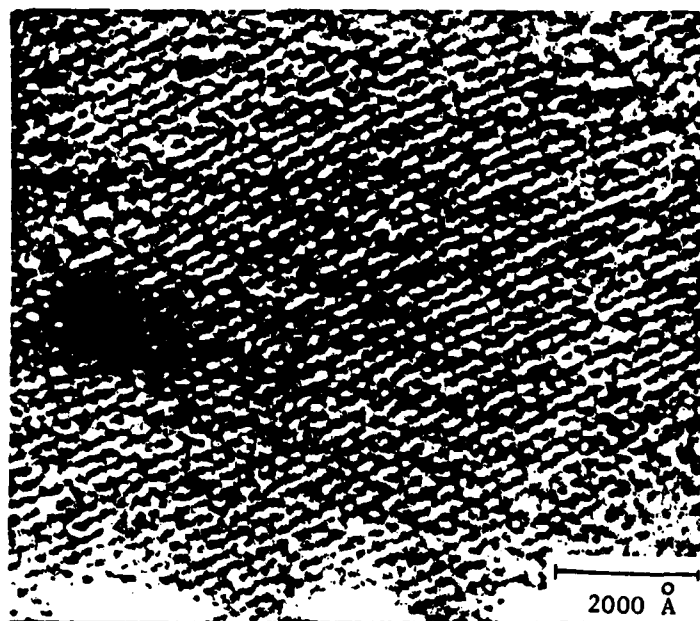Figure 6.   Electron Micrographs of the SBS Sample
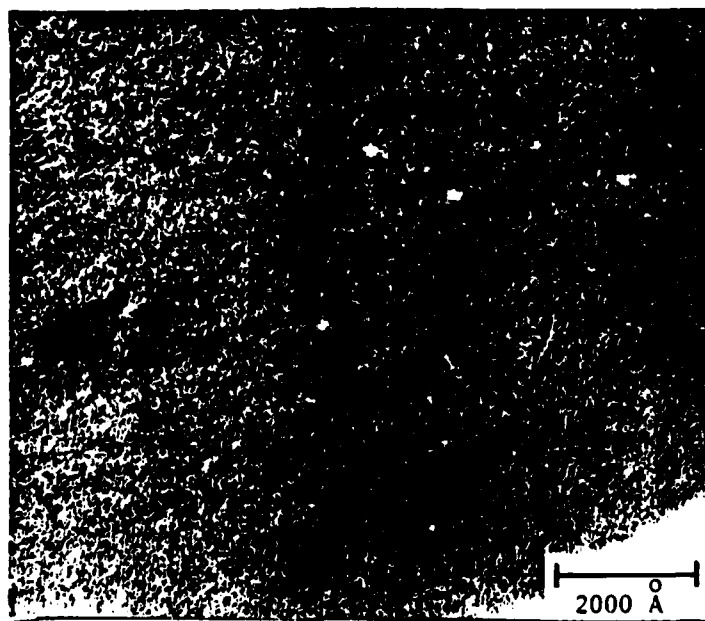   Annealed at 120°C.

Figure 7.   Electron Micrograph of the SBS Sample
Quenched from 125°C.

Figure 8.   Electron Micrograph of the SBS Sample
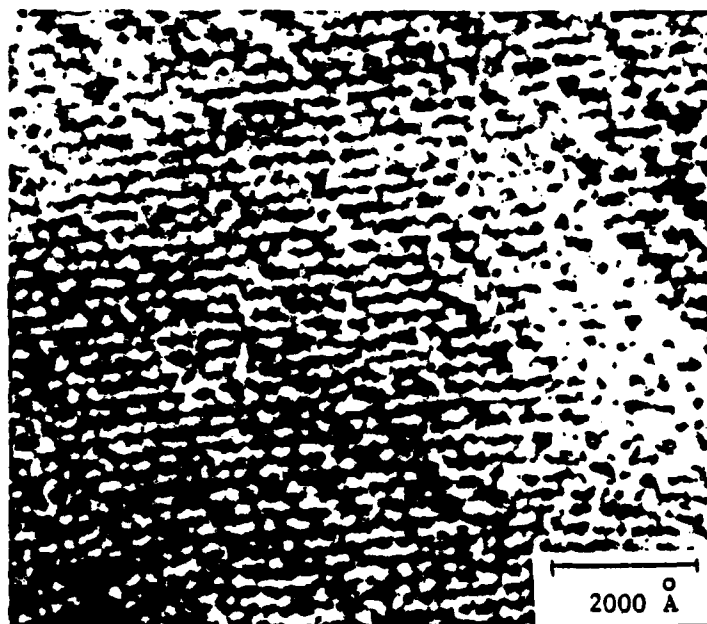Quenched from 170°C.

Figure 9. Electron Micrograph of SBS Sample Quenched
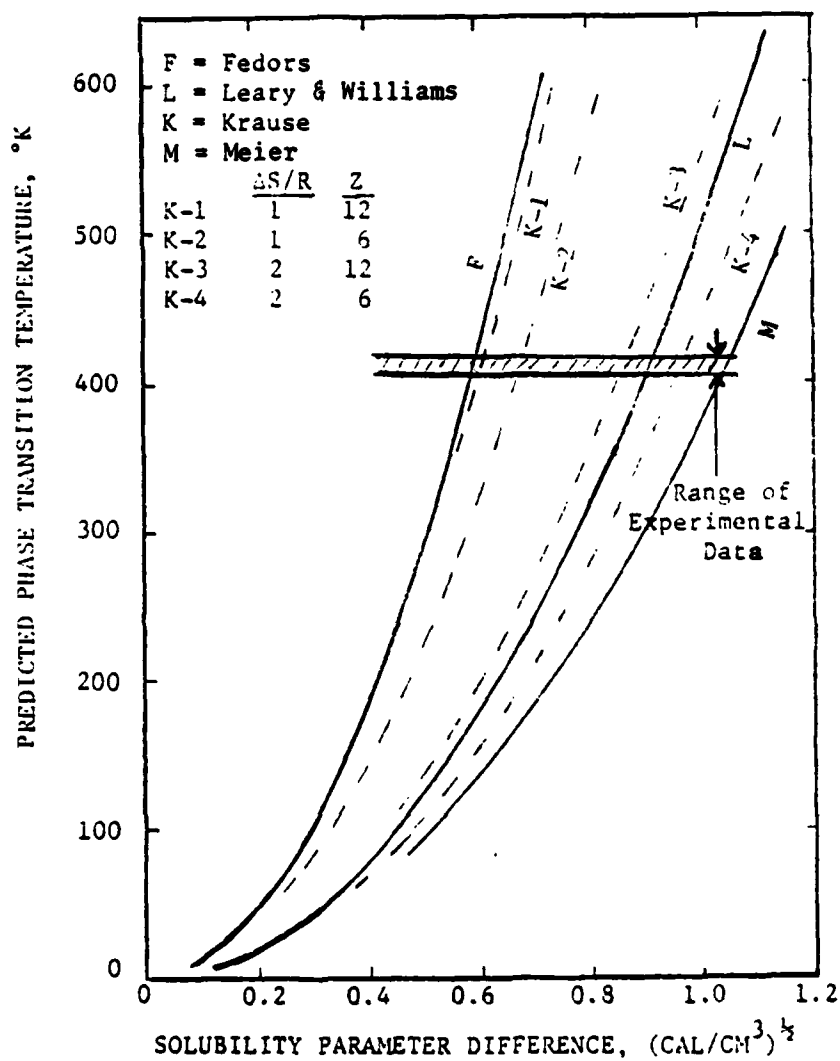From 190° and Annealed at 125°C.

FIGURE 10. Dependence of the Predicted Phase
Transition Temperatures on Solubility
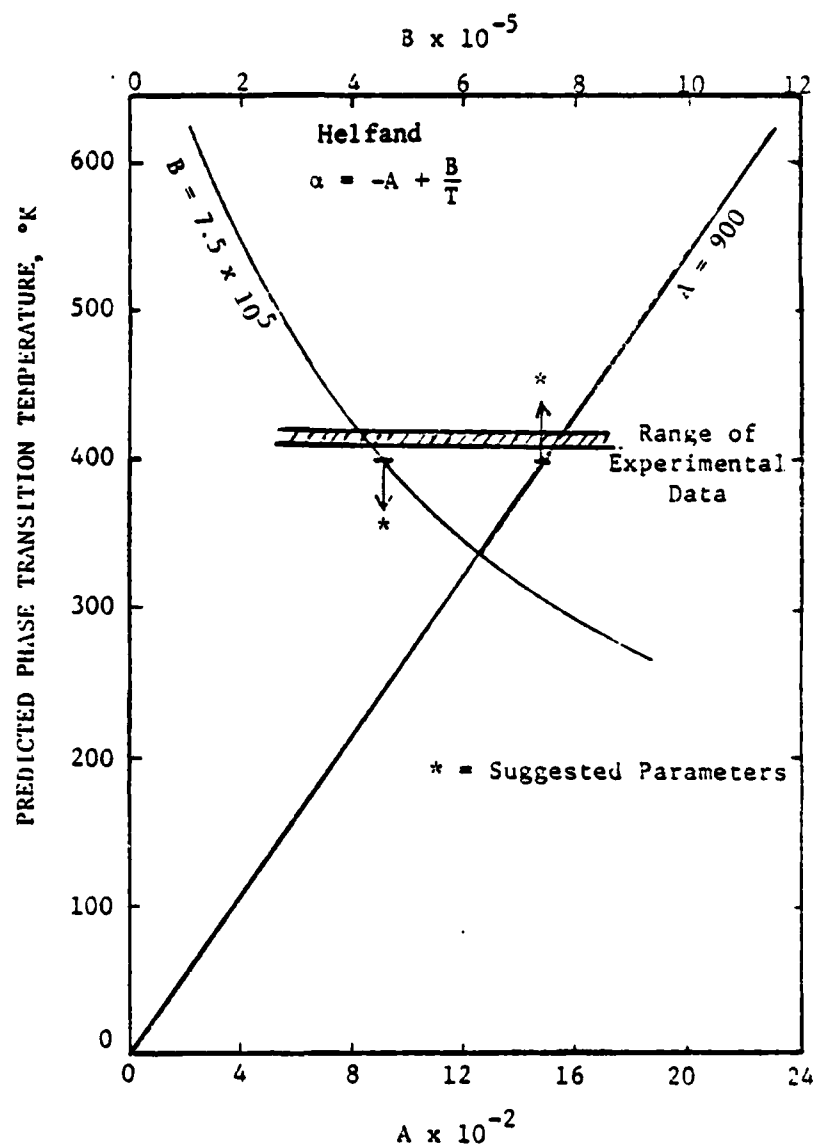Parameter Difference for 7S-43B-7S
Sample

FIGURE 11. Dependence of the Predicted Phase Transition
Temperature on Energy Parameters for
7S-43B-7S Sample

LIST OF THESES AND PUBLICATIONS

Ming-I. Lin, "The Precise Nature of the Melt Rheological Transition in a Styrene-Butadiene-Styrene Block Copolymer", Master of Engineering Thesis, R.P.I. (May, 1977)

Loretta Young, "A Study of the Morphological Transition in SBS Block Co-polymers", Master of Engineering Thesis, R.P.I. (February, 1979)

Henry L. Griesbach, "Melt Rheological Behavior of Two SBS Samples", Master of Science Thesis, R.P.I. (May, 1979)

Gary J.L. Johnson, "The Thermodynamics of the Morphological Transition in Triblock Copolymers", Master of Enginering Thesis, R.P.I. (December 1979)

C.I. Chung and J.C. Gale, J. Poly. Sci., Poly. Phys. Ed., 14, 1149 (1976)

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